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ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. SAMPLE TYPE VI, WATER-SURFACTANT

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

October 1959

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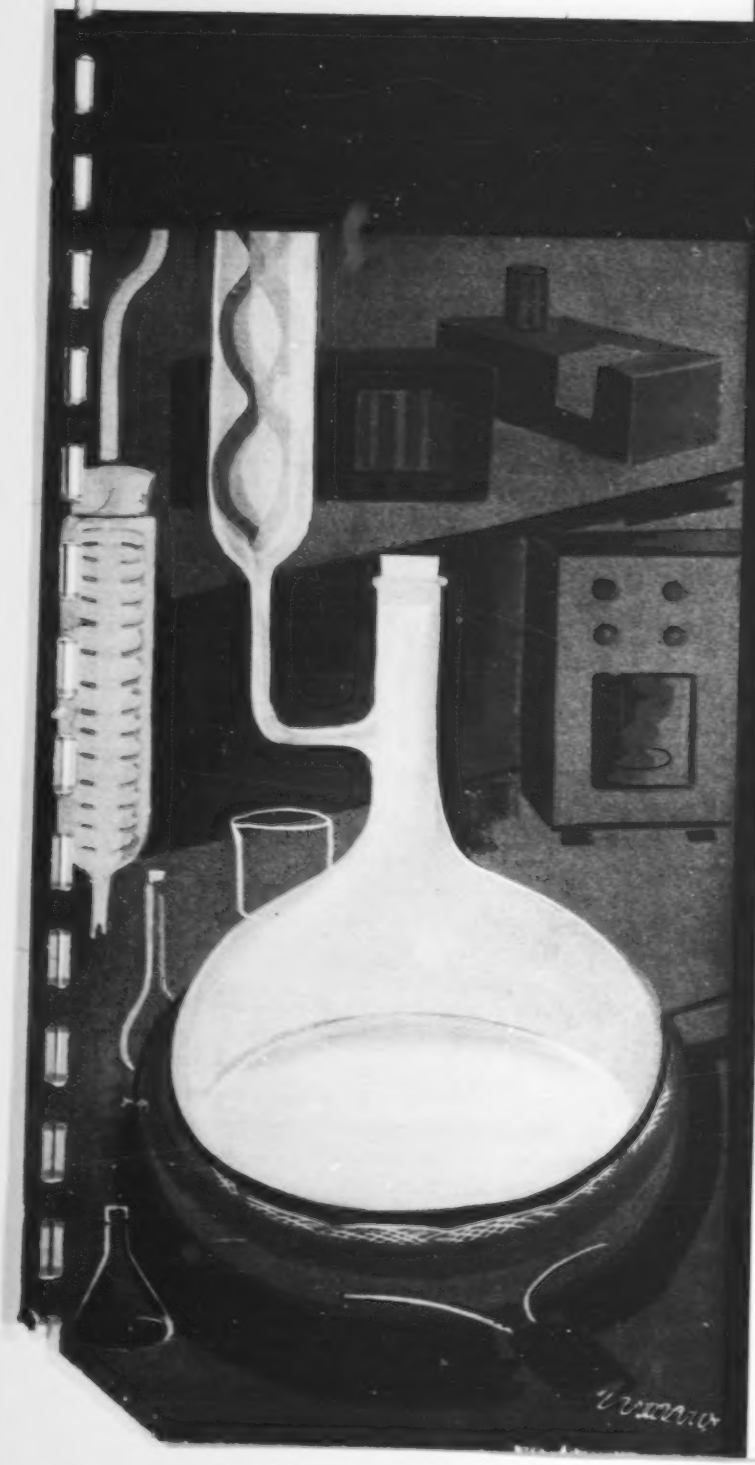
analytical reference service

sample type VI water-surfactant

October, 1959



training program

Robert A. Taft

Sanitary Engineering Center

Cincinnati, Ohio

U. S. Department of Health, Education, and Welfare

· Public Health Service

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NOTICE

Attention is called to the following errors that appeared in the Analytical Reference Service Report on Sample Type V (Water, Rad):

PAGE 2, line 7, change ± 0.5 to ± 0.03

TABLE 2

Agency #10 - change 4.81 to 4.68

Summary of Laboratory Procedures

Agency #5 - change 7.4, 7.6, 7.7 to 3.7, 3.8, 3.8
#10 - change 196, 198, 158 to 148, 140, 158
2.0, 2.0, 2.0 to 4.1, 3.9, 4.4
Agency #4 - change 11, 11, 11 to 5.5, 5.5, 5.5
#21 - change 1000 to 200

Summary of Instrumentation

Agency #1 - change 137 to 13.7
#10 - change 42 to 50

Summary of Counting

Agency #10 - change 500, 482, 548 to 480, 462, 526
change 4.50, 4.34, 4.94 to 4.33, 4.16, 4.74
change 4.71, 4.54, 5.17 to 4.60, 4.41, 5.03
change 4.81 to 4.68

These errors do not change the statistical evaluations of the report nor the final conclusions.

We wish particularly to amend the error in reporting the Oak Ridge National Laboratory result, since that group very graciously volunteered to assist in the evaluation of the sample.

ANALYTICAL REFERENCE SERVICE

INTRODUCTION

The Analytical Reference Service conducted by the Sanitary Engineering Center has as its primary goal the evaluation of laboratory methods in the field of sanitary engineering. The Reference Service itself is a voluntary association of member organizations responsible for the conduct of laboratory programs. The evaluations are obtained by the cooperative efforts of the members in the analysis of identical samples.

This mechanism provides:

1. A statistical evaluation of procedures, including precision and accuracy.

2. An opportunity for a participant to compare his laboratory procedures and results with other laboratories having similar responsibilities.

3. An exchange of information regarding weaknesses of currently approved methods.

4. Evidence regarding methods requiring further development or perhaps entirely new approaches.

5. A framework for broad-scale evaluation of new analytical methods.

PLAN OF OPERATION

Initially, efforts are being directed toward the chemical examination of water. The scope of the program will be broadened gradually to include other types of examinations and other media.

Using the most refined grade of chemicals available, samples are prepared containing measured amounts of the desired constituent. Decisions as to the qualitative makeup of any particular sample follow suggestions from the members and from the staff of the Sanitary Engineering Center.

After a sample is designed and prepared, a notice announcing its availability and qualitative makeup is sent with a self-addressed reply card to member organizations. An affirmative reply initiates immediate shipment of a portion of the described sample. Results are requested within some reasonable period, usually sixty days.

REPORTING OF RESULTS AND COMMENTS

Data are returned to the Sanitary Engineering Center on forms supplied with the sample. Space is provided on the forms for numerical values and a narrative critique of analytical procedures used.

The results obtained by the cooperating laboratories are compiled as in the accompanying report. From examination of the combined data, it is hoped that reliable estimates may be made of the accuracy and precision of the methods employed.

All laboratories are strongly encouraged to supply comments on the analytical methods they use. A complete log of pertinent details, including difficulties, modifications, sources of error, and other factors, is extremely valuable. Such a compilation of comments represents an exchange of ideas and opinions that is a significant part of the final report.

H P Kramer

H. P. Kramer
Chief, Training Program

ANALYTICAL REFERENCE SERVICE MEMBERS AS OF OCTOBER 1, 1959

State Agencies

Alabama Water Improvement Commission
Arizona State Department of Health
Arkansas State Board of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health
State of Hawaii Department of Health
Idaho State Board of Health
Illinois State Department of Health
Illinois State Water Survey Division
Kentucky State Department of Health
Louisiana State Health Department
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Michigan State Department of Health
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey Department of Health
New Mexico State Department of Public Health
New York State Department of Health
New York State Conservation Department
North Carolina State Board of Health
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
State of Rhode Island and Providence Plantations Dept. of Health
South Carolina State Water Pollution Control Authority
South Dakota Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Vermont State Water Conservation Board
Virginia State Department of Health
Virginia State Water Control Board
Washington State Department of Health
West Virginia State Water Commission

Municipal Agencies

Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
California Water Service Co. (San Jose)
Los Angeles County Flood Control District
Chicago Department of Water and Sewers
Flint Department of Public Works and Utilities
Dayton Department of Service and Buildings
Philadelphia Suburban Water Co.

Federal Agencies

Tennessee Valley Authority, Wilson Dam, Alabama (Lab I)
Tennessee Valley Authority, Wilson Dam, Alabama (Lab II)
Tennessee Valley Authority, Chattanooga, Tennessee
U.S. Dept. of the Interior, Geological Survey, Sacramento, Calif.
U.S. Dept. of the Interior, Geological Survey, Washington, D.C.
U.S. Dept. of the Interior, Geological Survey, Denver, Colorado
U.S. Dept. of the Interior, Geological Survey, Philadelphia, Pa.
U.S. Dept. of the Interior, Geological Survey, Columbus, Ohio
U.S. Dept. of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Army Environmental Health Laboratory, Maryland
Sanitary Engineering Division, 13th Naval District

Universities

Georgia Institute of Technology, Dept. of Applied Biology
Purdue University, Department of Chemistry
Rutgers University, Department of Sanitation
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
University of Pittsburgh, Graduate School of Public Health

Industry

National Aluminate Corporation
Monsanto Chemical Company
Ekroth Laboratories, Inc.
California Water Service Company

Foreign

Vancouver, B.C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare

PARTICIPANTS IN THIS STUDY OF SAMPLE TYPE VI

California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health
State of Hawaii Department of Health
Idaho State Board of Health
Illinois State Water Survey Division
Kentucky State Department of Health
Louisiana State Health Department
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Michigan State Department of Health
Minnesota State Department of Health
Montana State Board of Health
Nebraska State Department of Health
New Jersey Department of Health
New York State Department of Health
North Carolina State Board of Health
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
State of Rhode Island and Providence Plantations Dept. of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Vermont State Department of Health
Virginia State Water Control Board
West Virginia State Water Commission
Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Chicago Department of Water and Sewers
U.S. Dept. of the Interior, Geological Survey, Columbus, Ohio
U.S. Dept. of the Interior, Bureau of Reclamation, Denver, Colorado
U.S. Army Environmental Health Laboratory, Maryland
U.S. Dept. of the Interior, Geological Survey, Washington, D.C.
Georgia Institute of Technology, Dept. of Applied Biology
Rutgers University, Department of Sanitation
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
National Aluminate Corporation
Monsanto Chemical Company
West Virginia Pulp and Paper Company

LIST OF ANALYTICAL REFERENCE SERVICE SAMPLES WHICH HAVE BEEN DISTRIBUTED AND ON WHICH REPORTS HAVE BEEN COMPLETED

SAMPLE TYPE I AND I-A

(Mineral, Water) analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

SAMPLE TYPE II

(Heavy Metals, Water) analyzed for copper, cadmium, aluminum, chromium, iron, lead, manganese, and zinc.

SAMPLE TYPE III

(Fluoride, Water) analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLE TYPE IV

(Inorganics, Air) analyzed for chloride, sulfate, fluoride and nitrate in aqueous solution and on glass fiber hi-vol filter mats.

SAMPLE TYPE V

(Radiological, Water) analyzed for gross beta activity.

SAMPLES WHICH HAVE BEEN DISTRIBUTED AND WHICH ARE NOW IN THE PROCESS OF STUDY

SAMPLE TYPE VII

(Oxygen Demand, Water) to be analyzed for chemical and biochemical oxygen demand.

SAMPLE TYPE V-A

(Radiological, Water) in preparation, to be examined for gross beta activity.

REPORT ON SAMPLE TYPE VI

PURPOSE OF THIS STUDY

The tremendous increase in the use of synthetic detergents in the past 10 years has resulted in the frequent appearance of surface active agents in all types of waters - sewage, industrial wastes, surface and ground waters and even drinking waters. The ubiquitous nature of these surfactants, especially the anionics has led to a pressing need for efficient, reliable analytical procedures.

The original purpose of this study was to evaluate several current procedures on a variety of samples, but since the large majority of the cooperating agencies are using the same procedure, the study is essentially a survey of a single method. Further, the characteristics of the data are such that part of the final interpretation is devoted to sample behavior. Such was not the original purpose of this study but the pronounced bias of the data indicates existence of other factors not directly connected with analytical deficiencies.

PREPARATION AND COMPOSITION OF SAMPLE

Sample Type VI consisted of three individual solutions designated as A, B and C, dosed with a carefully measured amount of alkyl benzene sulfonate. Each solution represented water of a specific type and contained a different concentration of surfactant.

Solution A (distilled water) was representative of a sample with no interferences. Solution B (Cincinnati tap water) represented drinking water. Solution C (Ohio River water) represented raw water containing a moderate amount of turbidity and dissolved solids. The concentrations of active material were not intended to represent the levels usually encountered in the field.

Preliminary work by the Analytical Reference Service indicated that alkyl benzene sulfonate was completely stable in both distilled water and tap water. In order to insure stability for the river water, however, the substrate was settled, decanted, and autoclaved prior to addition of the surfactant. Since the pilot sample showed complete stability for more than 90 days, it was assumed that such measures would also insure stability in the actual sample.

The primary standard supplied to each cooperating agency with the sample was obtained from the American Association of Soap and Glycerine Manufacturers. This material was also used in the preparation of the sample to insure that the particular surface active agent measured was the same in both sample and standard.

The complete sample as distributed to each cooperating agency was composed of:

1) Three 2 liter water samples
2) A procedural outline for performing the ABS determination
3) A standardized report form
4) A portion of primary standard ABS and methylene blue dye

The concentration of active materials in the three samples was:

Distilled water	0.40 mg/l ABS
Cincinnati tap water	2.22 mg/l ABS
Ohio River water	1.31 mg/l ABS

TREATMENT OF DATA

Forty-two agencies cooperated in this study. Eight of these submitted results obtained by different analysts or by using comparative analytical procedures. These additional results are treated as from individual agencies so that 50 separate values for each part of the study are included in this report.

Forty-three of the 50 values reported are based on the same analytical method. No other method or modification was used more than twice, so that results from these methods are not significant and have no effect on the overall results. The data is therefore treated as if based on a single procedure. Further, since it is apparent that the type of instrument used for color measurement did not affect the results, this factor is not discussed in this report.

The data have been summarized by means of bar charts and probability papers. Conventional parameters have been used for analysis of the raw data, and are summarized in the appropriate sections of this report.

SOLUTION A - DISTILLED WATER

Solution A of this study was prepared by adding a solution of standard ABS to 46 liters of deionized distilled water to obtain a pre-selected concentration of 0.40 mg/l. This solution served as a standard for measurement of accuracy and precision in the absence of interfering materials. The mean, the median and the mode for 50 obersvations was 0.39 mg/l in each case. The distribution of the analytical results, however, was not normal, since 31 agencies reported low results and only 13 were high (Figure 1). Because this solution was, in practice, an actual standard without any known interferences, similar losses should have been experienced in the preparation of standard curves, thereby cancelling the negative tendency observed in the histogram. In the absence of any apparent reason for the low skewed results, it may be assumed that the most probable concentration of ABS in Solution A was actually 0.39, and not 0.40 mg/l. From consideration of the physical nature of the primary standard and the method of sample preparation, such an assumption (an error of 0.01 mg/l of ABS) would not be unreasonable.

To test the plausibility of this reasoning, the histogram was redrawn with the base line indicated at 0.39 mg/l of ABS. The resultant figure exhibited a more normal distribution of the data with no pronounced skewness.

Regardless of the true concentration of active material in the solution, the precision and accuracy of the measurements performed on this sample were excellent. Assuming 0.39 mg/l of ABS to be the true concentration, 7 agencies submitted perfect results and 10 others obtained concentrations within $\pm$ 0.01 mg/l of this amount. Half of all the cooperating agencies obtained results within $\pm$ 0.04 mg/l of the mean.

SUMMARY OF RESULTS - SOLUTION A

Number of observations	50
Amount of ABS added	0.40 mg/l
Most probable concentration	0.39 mg/l
Mean	0.39 mg/l
Median	0.39 mg/l
Standard deviation from mean	$\pm$0.07 mg/l
95% Confidence Limit	$\pm$0.14 mg/l
50% Confidence Limit	$\pm$0.04 mg/l
Range	0.25 - 0.63 mg/l

SUMMARY OF RESULTS

PART A - 0.40 mg/l

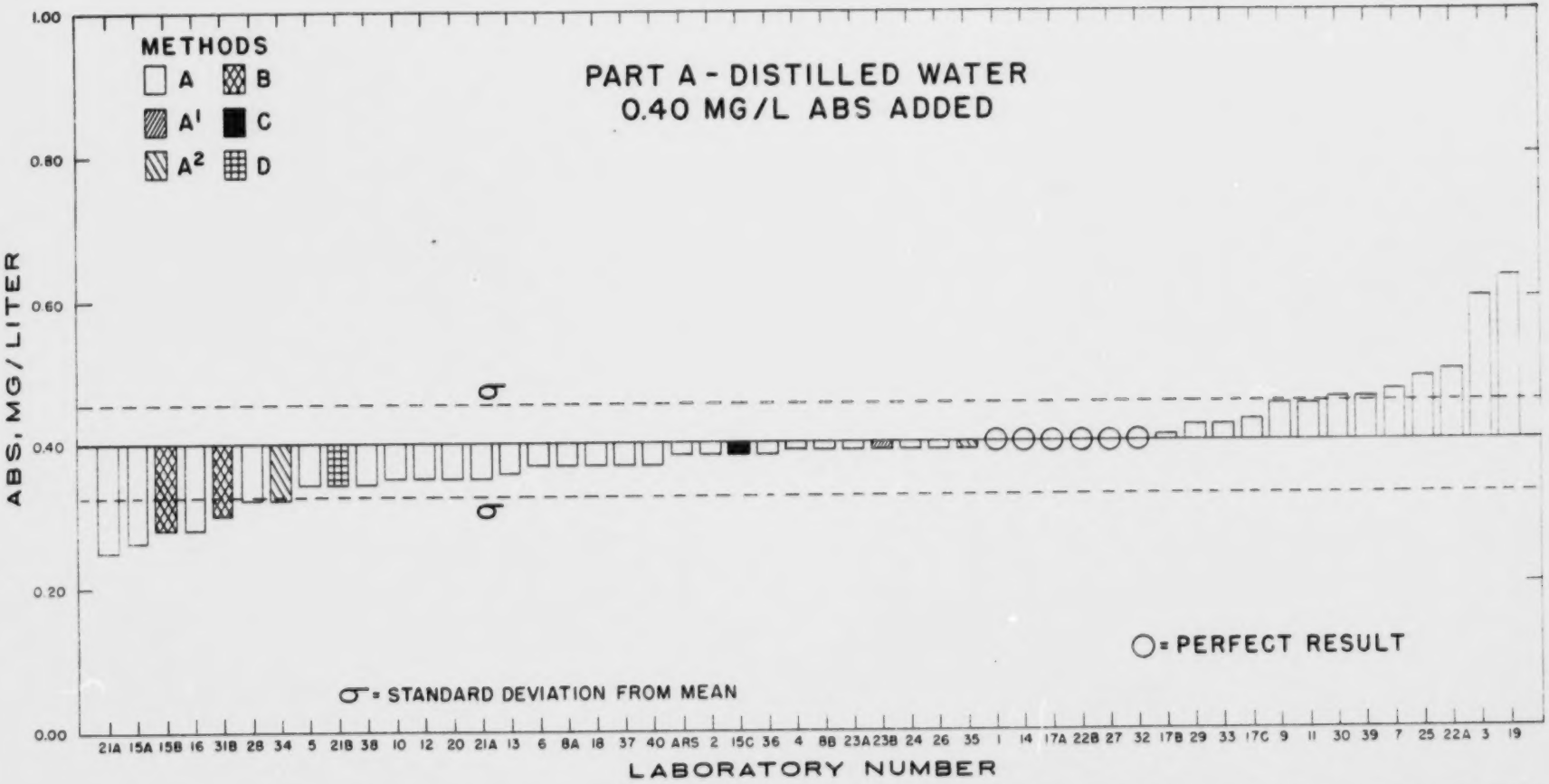
Lab No.	Results	Mean	% Recovery	Method
31A	0.25 0.24 0.25	0.25	62.5	A
15A	0.32 0.23 0.23	0.26	65.0	A
15B	0.25 0.29 0.30	0.28	70.0	B
16	0.26 0.30 0.29	0.28	70.0	A
31B	0.30 ---- ----	0.30	75.0	B
28	0.31 0.33 0.32	0.32	80.0	A
34	0.30 0.34 0.33	0.32	80.0	A[2]
5	0.34 0.35 0.34	0.34	85.0	A
21B	0.34 ---- ----	0.34	85.0	D
38	0.27 0.36 0.39	0.34	85.0	A

Lab. No:	Results	Mean	% Recovery	Method
10	0.36 0.35 0.35	0.35	88.5	A
12	0.34 0.34 0.36	0.35	88.5	A
20	0.30 0.38 0.38	0.35	88.5	A
21A	0.37 0.34 0.34	0.35	88.5	A
13	0.37 0.33 0.38	0.36	90.0	A
6	0.36 0.36 0.40	0.37	92.5	A
8	0.38 0.38 0.35	0.37	92.5	A
18	0.36 0.37 0.37	0.37	92.5	A
37	0.32 0.38 0.41	0.37	92.5	A
40	0.39 0.35 0.38	0.37	92.5	A
ARS	0.36 0.39 0.39	0.38	95.0	A

Lab No.	Results	Mean	% Recovery	Method
2	0.37 0.40 0.38	0.38	95.0	A
15C	0.38 0.38 ----	0.38	95.0	C
36	0.36 0.40 ----	0.38	95.0	A
4	0.38 0.39 0.39	0.39	97.5	A
8A	0.38 0.40 0.39	0.39	97.5	A
23A	0.39 0.39 0.40	0.39	97.5	A
23B	0.39 0.39 0.39	0.39	97.5	A[1]
24	0.38 0.42 0.38	0.39	97.5	A
26	0.43 0.33 0.40	0.39	97.5	A
35	0.39 0.39 0.39	0.39	97.5	A[2]
1	0.40 0.40 0.40	0.40	100.0	A

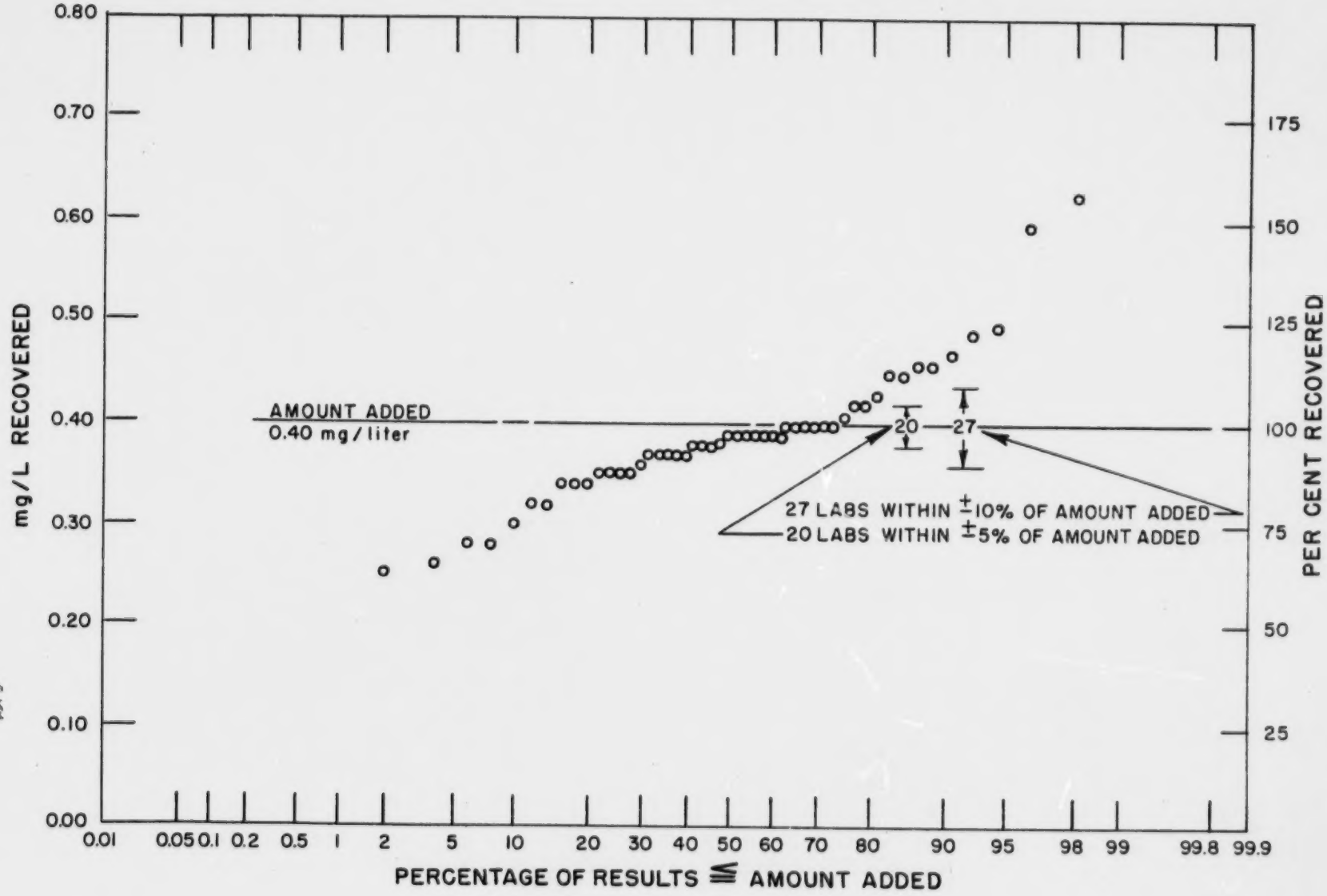
Lab No.	Results	Mean	% Recovery	Method
14	0.40 0.40 0.40	0.40	100.0	A
17A	0.41 0.40 0.40	0.40	100.0	A
22B	0.40 ---- ----	0.40	100.0	A
27	0.43 0.38 0.38	0.40	100.0	A
32	0.40 0.40 0.40	0.40	100.0	A
17B	0.42 0.40 0.41	0.41	102.5	A
29	0.43 0.40 ----	0.42	105.0	A
33	0.40 0.43 0.43	0.42	105.0	A
17C	0.41 0.44 0.44	0.43	107.5	A
9	0.44 0.46 0.46	0.45	112.5	A
11	0.42 0.48 0.45	0.45	112.5	A

Lab No.	Results	Mean	% Recovery	Method
30	0.46 0.47 0.46	0.46	115.0	A
39	0.48 0.46 0.45	0.46	115.0	A
7	0.46 0.47 0.48	0.47	117.5	A
25	0.47 0.50 0.50	0.49	122.5	A
22A	0.50 ---- ----	0.50	125.0	A
3	0.65 0.70 0.45	0.60	150.0	A
19	0.64 0.64 0.62	0.63	157.5	A


METHODS
A
B
A¹
C
A²
D
PART A - DISTILLED WATER
0.40 MG/L ABS ADDED
1.00
0.80
0.60
0.40
0.20
0.00
ABS, MG/LITER
σ
σ
○ = PERFECT RESULT
σ = STANDARD DEVIATION FROM MEAN
21A 15A 15B 16 31B 28 34 5 21B 38 10 12 20 21A 13 6 8A 18 37 40 ARS 2 15C 36 4 8B 23A 23B 24 26 35 1 14 17A 22B 27 32 17B 29 33 17C 9 11 30 39 7 25 22A 3 19
LABORATORY NUMBER

ANALYTICAL REFERENCE SERVICE - SAMPLE TYPE VI (WATER, SURFACTANT)

FIGURE 1



SAMPLE TYPE VI
PART A

SOLUTION B - CINCINNATI TAP WATER

In the preparation of Solution B of this sample, Cincinnati tap water was examined for residual or apparent residual ABS which replicate examinations showed to be 0.12 mg/l. Standard ABS was then added to yield a concentration of 2.22 mg/l.

As with Solution A, 50 individual results were returned. The mean, the median and the mode were respectively 2.14, 2.10 and 2.10 mg ABS/l. Examination of the histogram (Figure 2) again shows low skewed results but in this case the apparent loss of ABS is more pronounced. Reconstruction of the histogram, assuming an error of 0.05 mg/l ABS, (5 times the error in Solution A) did not significantly change the overall tendency toward low results. Before reconstruction of the chart, 39 members obtained low results; after adjustment of the base line, 34 obtained less than 100% recovery.

Why this apparent loss of ABS in the sample occurred is not known. Several assumptions may be made but the true explanation may be reached only through further study. Loss of ABS, however, might be attributed to the following:

1) Presence of naturally occurring interferers in the substrate water, which could be a function of the mineral content of the water.

2) Irreversible adsorption of ABS molecules on solid surfaces such as vessel walls or turbidity particles, preventing reaction with methylene blue.

3) Biological degradation of ABS by organisms surviving water treatment processes or organisms introduced after sample preparation.

It is interesting to note that in spite of the consistent loss of ABS as indicated in the bar charts, the analytical procedures still furnish excellent results. The mean recovery for all 50 laboratories was 92%, with a standard deviation from the mean of only $\pm$ 0.18 mg/l. Half of all the cooperating agencies obtained results within $\pm$ 0.13 mg/l.

SUMMARY OF RESULTS - SOLUTION B

Number of Observations	50
Amount of ABS added	2.22 mg/l
Mean	2.14 mg/l
Median	2.10 mg/l
Standard deviation from mean	±0.18 mg/l
95% Confidence limit	±0.36 mg/l
50% Confidence limit	±0.14 mg/l
Range	1.65 - 2.70 mg/l

SUMMARY OF RESULTS

PART B - 2.22 mg/l

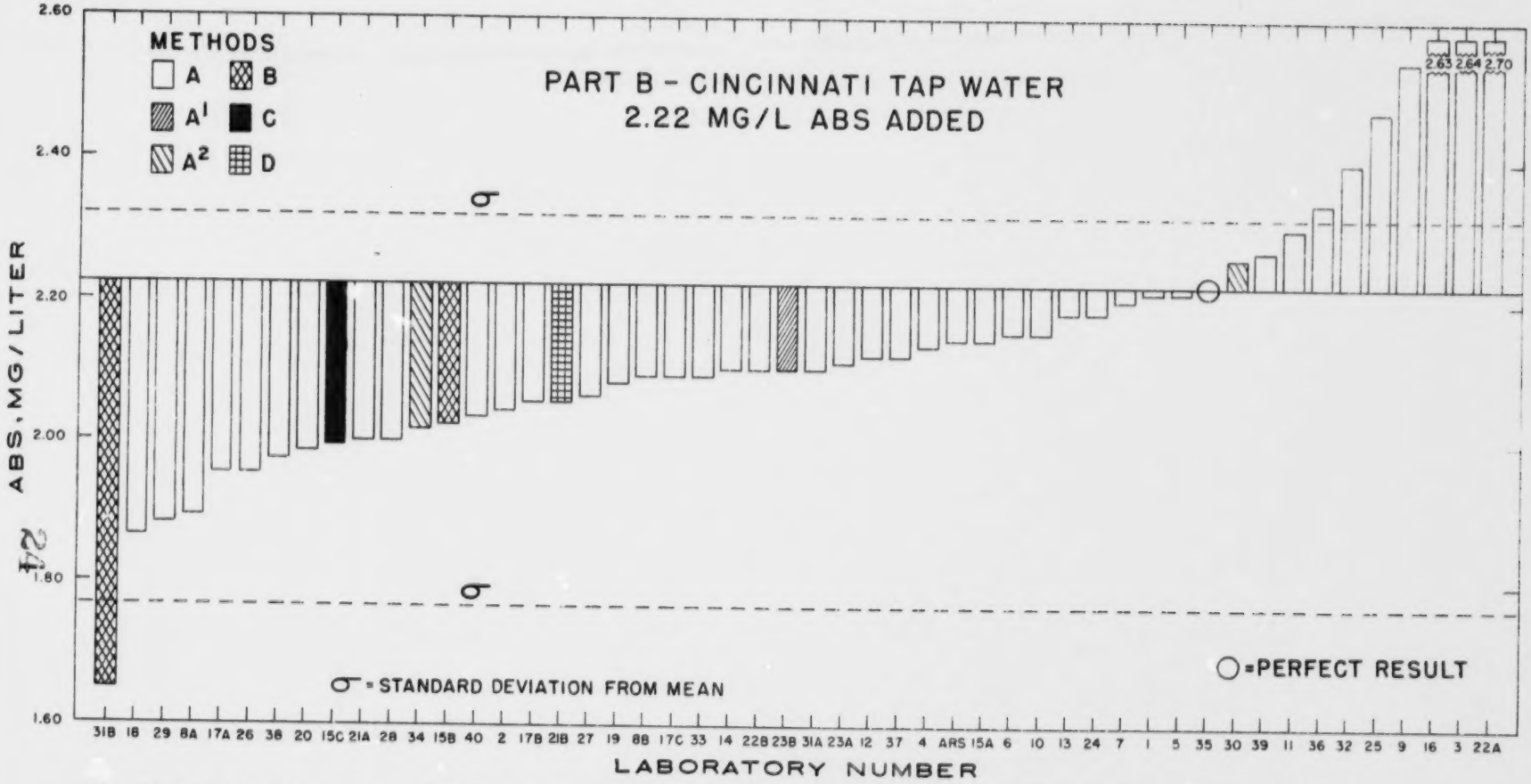
Lab No.	Results	Mean	% Recovery	Method
31B	1.65 ---- ----	1.65	74.3	B
18	1.89 1.86 1.78	1.84	82.9	A
29	1.80 1.86 1.98	1.88	84.7	A
8	1.78 1.80 2.10	1.89	85.1	A
17A	1.92 1.96 1.96	1.95	87.8	A
26	1.93 1.95 1.98	1.95	87.8	A
38	1.76 1.96 2.20	1.97	88.7	A
20	2.11 1.94 1.88	1.98	89.2	A
15C	1.96 2.04 1.96	1.99	89.7	C
21A	1.98 2.00 2.01	2.00	90.1	A

Lab No.	Results	Mean	% Recovery	Method
28	1.99 2.01 1.99	2.00	90.1	A
34	2.02 2.00 2.02	2.01	90.5	A[2]
15B	2.00 2.00 2.05	2.02	91.0	B
40	2.04 2.00 2.04	2.03	91.4	A
2	2.25 1.93 1.93	2.04	92.0	A
17B	2.00 2.06 2.08	2.05	92.3	A
21B	2.05 ---- ----	2.05	92.3	D
27	2.01 2.07 2.11	2.06	92.8	A
19	2.10 2.14 2.01	2.08	93.7	A
8A	2.09 2.09 2.09	2.09	94.3	A
17C	2.04 2.11 2.13	2.09	94.3	A

Lab No.-	Results	Mean	% Recovery	Method
33	2.10 2.07 2.10	2.09	94.3	A
14	2.00 2.20 2.20	2.10	94.7	A
22B	2.10 ---- ----	2.10	94.7	A
23B	2.25 2.08 1.98	2.10	94.7	A[1]
31A	2.09 2.14 2.06	2.10	94.7	A
23A	2.18 1.98 2.18	2.11	95.0	A
12	2.08 2.19 2.08	2.12	95.5	A
37	2.12 2.03 2.20	2.12	95.5	A
4	2.13 2.13 2.12	2.13	95.8	A
ARS	2.16 2.12 2.14	2.14	96.4	A
15A	2.17 2.19 2.07	2.14	96.4	A

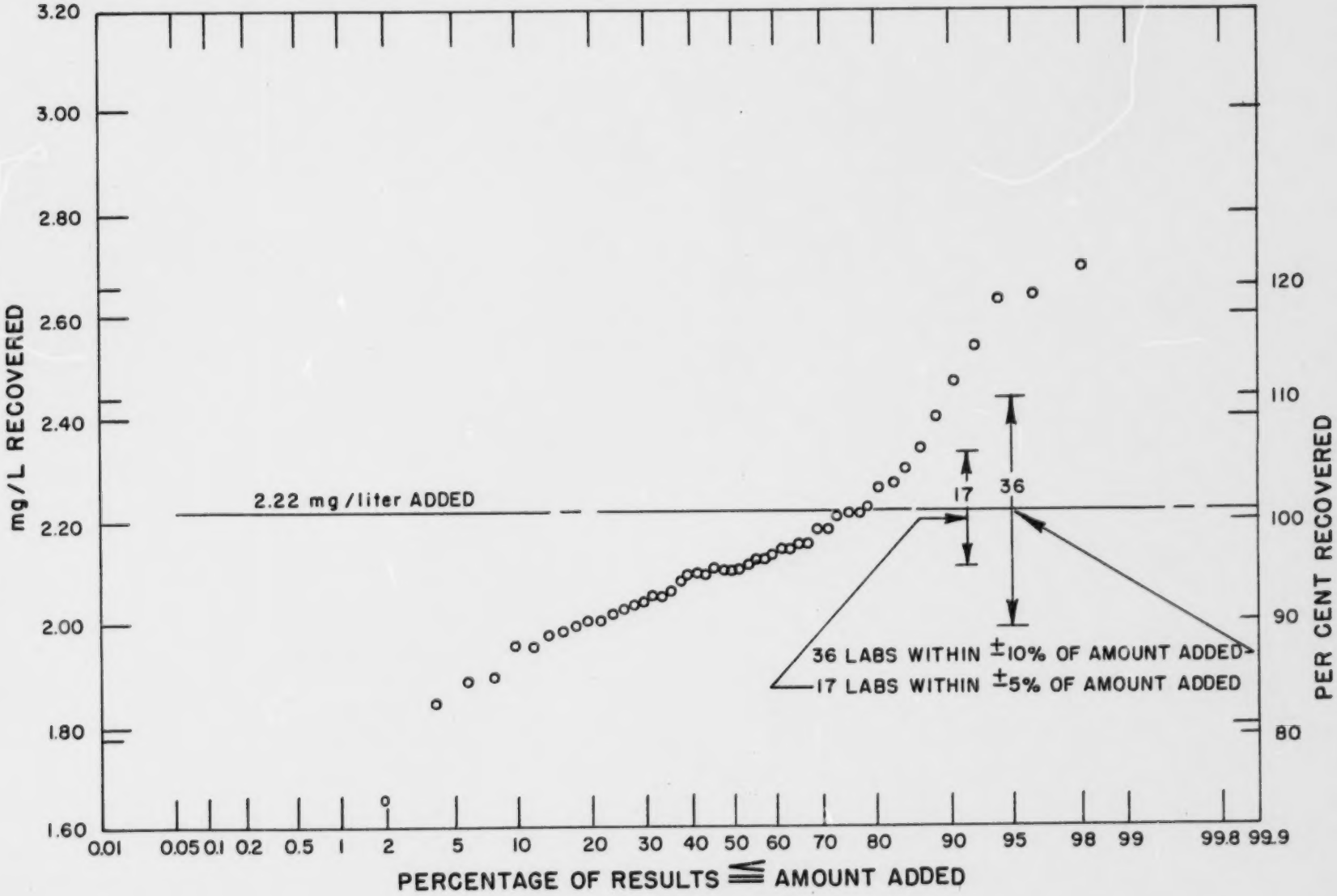
Lab No.	Results	Mean	% Recovery	Method
6	2.13 2.13 2.18	2.15	96.8	A
10	2.09 2.19 2.19	2.15	96.8	A
13	2.20 2.18 2.16	2.18	98.3	A
24	2.06 2.17 2.32	2.18	98.3	A
7	2.21 2.20 2.20	2.20	99.2	A
1	2.20 2.12 2.30	2.21	99.5	A
5	2.21 2.21 2.21	2.21	99.5	A
35	2.22 2.22 2.22	2.22	100.0	A[2]
30	2.28 2.24 2.26	2.26	101.8	A
39	2.23 2.23 2.35	2.27	102.3	A
11	2.32 2.28 2.30	2.30	103.5	A

Lab No.	Results	Mean	% Recovery	Method
36	2.34 2.34 ----	2.34	105.4	A
32	2.40 2.40 2.40	2.40	108.1	A
25	2.44 2.47 2.50	2.47	111.3	A
9	2.59 2.43 2.61	2.54	114.2	A
16	2.51 2.71 2.66	2.63	118.3	A
3	3.08 2.60 2.24	2.64	119.0	A
22A	2.70 ---- ----	2.70	121.6	A



ANALYTICAL REFERENCE SERVICE - SAMPLE TYPE VI (WATER, SURFACTANT)

FIGURE 2



SAMPLE TYPE VI
PART B

SOLUTION C - OHIO RIVER WATER

Solution C was prepared by allowing a large volume of Ohio River water to settle for 24 hours, after which the supernatant, containing slight color and turbidity, was carefully withdrawn and autoclaved for 15 minutes at 121°C. After cooling, the sample was examined for residual surfactant and standard ABS added to give a concentration of 1.31 mg/l. No subsequent effort was made to maintain sterility of the substrate, since preliminary work on the pilot sample, under similar conditions, had indicated complete stability of ABS for more than 90 days.

As with Solutions A and B, the results were uniformly low, with 45 out of 50 agencies obtaining less than 100% recovery. Since the concentration in Solution C was approximately 3 times that in A, a negative error of 0.03 mg/l was assumed. After replotting the bar chart for this series, 43 members still exhibited low results.

In this series, the effect of aging on recovery was examined statistically and is shown graphically in Figure 4. For the 25 agencies completing the work within 20 days or less after sample shipment, the mean result was 1.20 mg/l. Similarly, the mean of 25 groups completing the work more than 20 days after shipment was 1.05 mg/l. It appears from these results that loss of active material was a function of time. The loss may be ascribed to biological activity resulting from post contamination of the sample. It is possible that this same factor may have influenced the results for Solutions A and B.

In contrast, however, to Solutions A and B which had a mean recovery for all groups of 97 and 92% respectively, Solution C showed a mean recovery of only 86% with a standard deviation of ± 0.205 mg/l.

SUMMARY OF RESULTS - SOLUTION C

Number of observations	50
Amount of ABS added	1.31 mg/l
Mean	1.13 mg/l
Median	1.10 mg/l
Standard deviation from mean	±0.20 mg/l
95% Confidence limit	±0.41 mg/l
50% Confidence limit	±0.14 mg/l
Range	0.75 - 2.00 mg/l

SUMMARY OF RESULTS

PART C - 1.31 mg/l

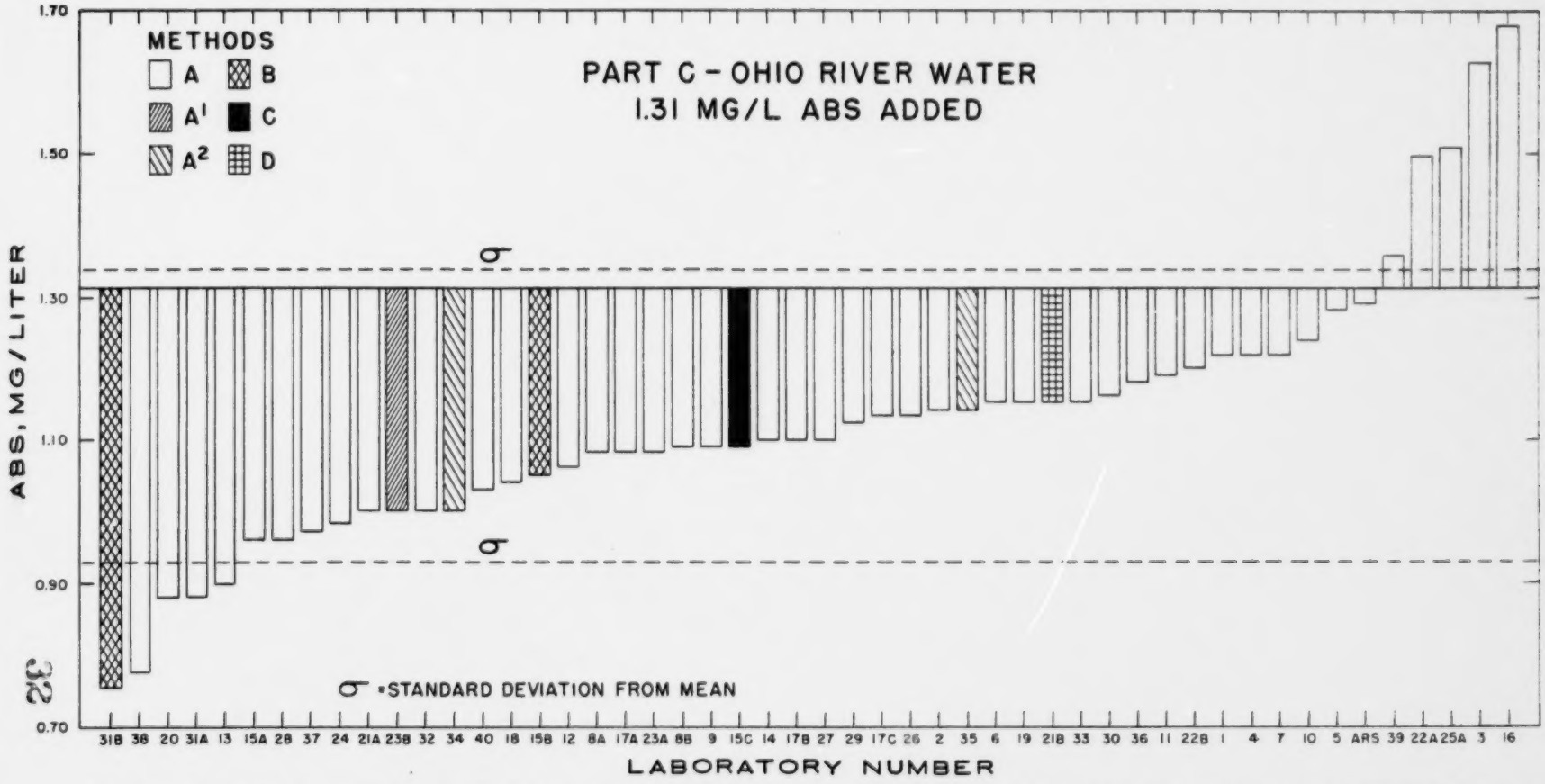
Lab No.	Results	Mean	% Recovery	Method
31B	0.75 ---- ----	0.75	57.3	B
38	0.68 0.80 0.82	0.77	58.8	A
20	0.93 0.87 0.84	0.88	67.2	A
31A	0.88 0.91 0.84	0.88	67.2	A
13	0.87 0.89 0.94	0.90	68.7	A
15A	0.96 0.96 ----	0.96	73.3	A
28	0.93 0.99 0.97	0.96	73.3	A
37	0.95 0.96 1.00	0.97	74.0	A
24	0.89 1.06 0.99	0.98	74.8	A
21A	1.04 0.99 0.96	1.00	76.3	A

Lab No.	Results	Mean	% Recovery	Method
23B	1.00 1.00 1.00	1.00	76.3	A[1]
32	1.00 1.00 1.00	1.00	76.3	A
34	0.98 1.01 1.00	1.00	76.3	A[2]
40	1.02 1.04 1.02	1.03	78.6	A
18	1.03 1.08 1.01	1.04	79.4	A
15B	1.05 1.05 1.05	1.05	80.2	B
12	1.04 1.04 1.09	1.06	80.9	A
8	1.07 1.10 1.07	1.08	82.4	A
17A	1.16 1.02 1.06	1.08	82.4	A
23A	1.07 1.08 1.09	1.08	82.4	A
8A	1.15 1.12 1.00	1.09	83.3	A

Lab No.	Results	Mean	% Recovery	Method
9	1.06 1.08 1.12	1.09	83.3	A
15C	1.10 1.12 1.06	1.09	83.3	C
14	1.10 1.10 1.10	1.10	84.0	A
17B	1.16 1.06 1.08	1.10	84.0	A
27	1.12 1.06 1.11	1.10	84.0	A
29	1.10 1.14 ----	1.12	85.5	A
17C	1.10 1.10 1.16	1.12	85.5	A
26	1.15 1.10 1.13	1.13	86.3	A
2	1.14 1.14 1.14	1.14	87.0	A
35	1.14 1.14 1.14	1.14	87.0	A[2]
6	1.09 1.22 1.15	1.15	87.8	A

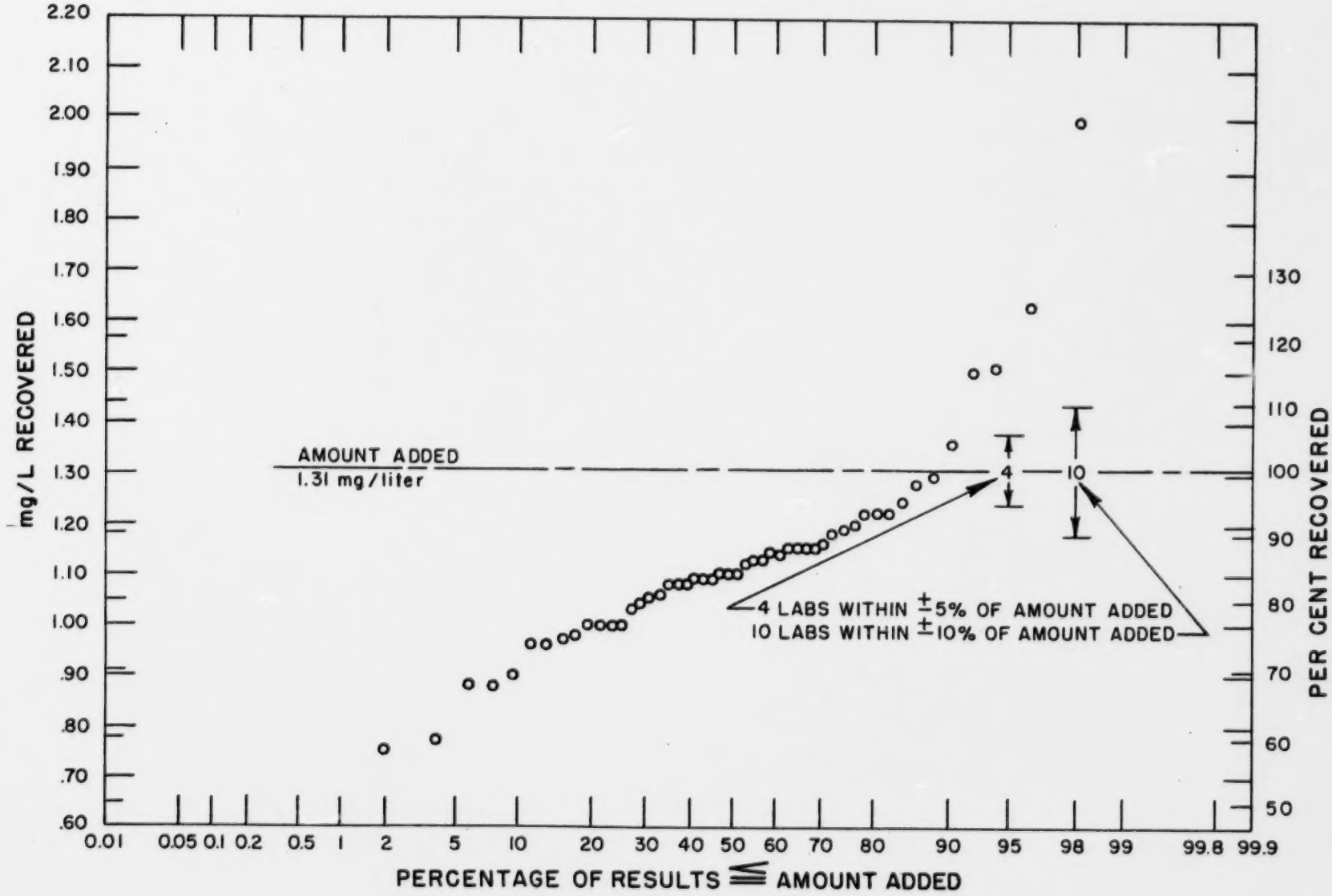
Lab No.	Results	Mean	% Recovery	Method
19	1.13 1.17 1.16	1.15	87.8	A
21B	1.15 ---- ----	1.15	87.8	D
33	1.10 1.20 1.15	1.15	87.8	A
30	1.22 1.15 1.12	1.16	88.5	A
36	1.20 1.18 1.18	1.18	90.1	A
11	1.18 1.15 1.24	1.19	90.8	A
22B	1.20 ---- ----	1.20	91.6	A
1	1.20 1.20 1.25	1.22	93.2	A
4	1.26 1.28 1.12	1.22	93.2	A
7	1.20 1.22 1.24	1.22	93.2	A
10	1.24 1.24 1.24	1.24	94.7	A

Lab No.:	Results	Mean	% Recovery	Method
5	1.16 1.30 1.30	1.25	95.6	A
ARS	1.29 1.28 1.29	1.29	98.5	A
39	1.36 1.36 1.36	1.36	103.8	A
22A	1.50 ---- ----	1.50	114.5	A
25	1.50 1.50 1.53	1.51	115.3	A
3	1.85 1.63 1.42	1.63	124.5	A
16	2.16 1.87 1.97	2.00	153.0	A

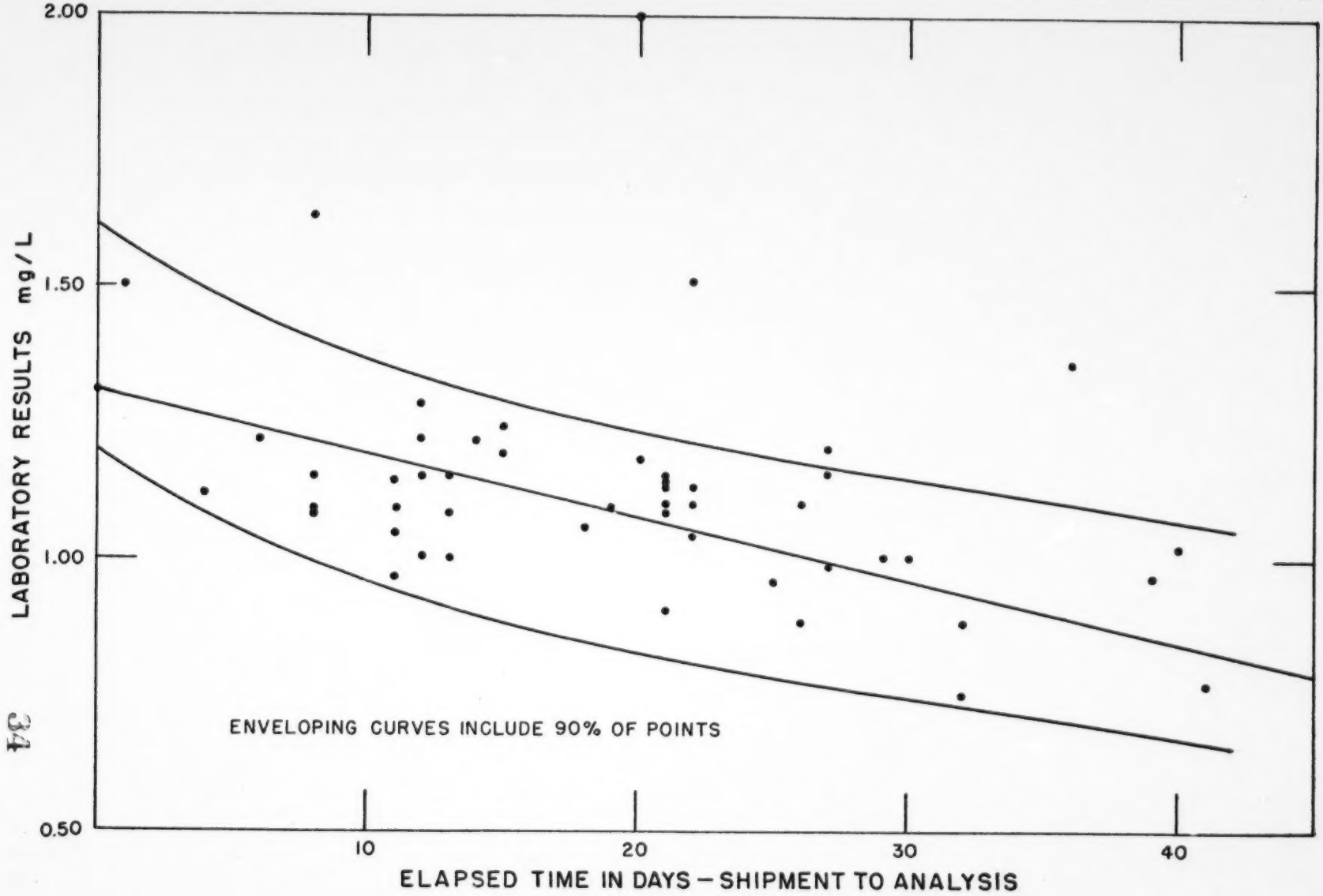

METHODS
A
B
A¹
C
A²
D
PART C - OHIO RIVER WATER
1.31 MG/L ABS ADDED
ABS, MG/LITER
1.70
1.50
1.30
1.10
0.90
0.70
σ
σ
σ = STANDARD DEVIATION FROM MEAN
31B 38 20 31A 13 15A 28 37 24 21A 23B 32 34 40 18 15B 12 8A 17A 23A 8B 9 15C 14 17B 27 29 17C 26 2 35 6 19 21B 33 30 36 11 22B 1 4 7 10 5 ARS 39 22A 25A 3 16
LABORATORY NUMBER

ANALYTICAL REFERENCE SERVICE - SAMPLE TYPE VI (WATER, SURFACTANT)

FIGURE 3



SAMPLE TYPE VI
PART C



SAMPLE TYPE VI
PART C – 1.31 mg/L ABS
EFFECT OF TIME ON ABS RECOVERY

SUMMARY AND CONCLUSIONS

Three separate solutions, comprising Sample Type VI, each containing carefully measured amounts of ABS were distributed to 42 members of the Analytical Reference Service. In this study, a total of 150 individual determinations were performed on each of these solutions.

Examination of the results shows a definite trend toward loss of ABS not attributable to error in preparation of the samples. Ninety percent of the members reported low results. The deficit is more pronounced in natural river water than in tap water or distilled water, although both of the latter indicate some loss.

The disappearance of the anionic material may be due to presence of interfering materials, adsorption on solid surfaces, biological action or a combination of all three. In any event, the diminution of ABS content appears to be a function of time which suggests that the analytical determinations routinely applied to waters of various natures yield minimum values. The values appear to be related to the nature of the water and the duration of residence of the ABS therein.

COMMENTS

Lab 1 Procedure is rapid and works very well. It is very adaptable to routine analysis.

Lab 2 No comments.

Lab 3 This laboratory has used the Methyl Green method as described in Anal. Chem. 28, No. 2 - p. 161 - Feb. '56 and has found it to go much smoother than this procedure.

Lab 4 We find this method easy to use with good precision.

Lab 5 Method shows good accuracy and reproducibility. We would prefer a water wash in place of the filtration step and reading the sample against an extracted blank, rather than against chloroform. We found that a quaternary, such as tetra-n-butyl ammonium hydroxide quantitatively ties up the anionic material and could be used in the preparation of a blank.

Lab 6 In using this method for samples with a concentration of less than 0.2 ppm, we found that reproducibility was not too good and that the percentage of error was consequently rather large.

Lab 7 We do not run ABS routinely. Standard curve was satisfactory. Method afforded no apparent manipulative difficulties. Phase separation was clean.

Lab 8 No comments.

Lab 9 The standard curve obtained was a straight line only up to a concentration of approximately .04 mg of ABS standard. Above this point, the slope changed rapidly.

Lab 10 No comments.

Lab 11 No comments.

Lab 12 No comments.

Lab 13 Best results obtained in lower ranges. Fifty ml aliquot used on portion B.

Lab 14 Surfactant determinations are not routinely made by this laboratory. The procedure seems to be satisfactory. It was noted that the points of the standard curve did not form a straight line throughout the suggested range of concentration. It was also noted that the methylene blue dye caused considerable staining of the glassware.

Lab 15A Methylene blue apparently absorbed in varying amounts during shaking. It appears that precise duplication of shaking is required for each sample.

Lab 15B Fastest of 3 methods tested. Precision was good on samples B and C.

Lab 15C Longest of 3 methods tested.

Lab 16 No comments.

Lab 17A We like this method very much, especially as one doesn't have to wash
17B the chloroform. Checks very well with Proctor & Gamble's standard
17C ABS 41% which we have on hand.

Factor OD/ppm = 0.47 on SEC Standard
Factor OD/ppm = 0.45 on P&G Standard

Lab 18 We do not customarily measure anionic surfactants in our laboratory, so the procedural outline submitted with the samples was used. However, we have some doubt as to the specificity of this method for waste streams. We would like to suggest investigation of a more specific method, which is not subject to any known interferences.

Lab 19 Method straightforward and typical of extraction methods in general. Color in sample B a little insidious in manner in which it adhered to side of flask. We modified procedure by inserting pledgets of cotton into stem of separatory funnel instead of using a separate funnel and cotton filter.

Lab 20 This method is much the same as the one we use routinely. However, we use filter paper in place of cotton. Visually, the cotton seems to remove more color from the extracts, especially in the high concentrations. The samples were not refrigerated immediately, but stood for some time at room temperature. It will be noted that our 2.5 mg/l standard gives a reading considerably off from a straight line. Due to the press of other work, it was not feasible to run a check at this time. This does not appreciably affect the sample results, however.

We do not understand the deviation from the straight line shown by the calibration curve around the origin. Most of the time we have obtained good straight calibration curves using this method. Perhaps the use of cotton has an effect greater than that of filter paper in the lower concentrations.

Lab 21 We found this method preferable to the method we have been using because of its reproducibility, simplicity of analysis and stability of reagents. We have been using our own modification of Evans Method. Results on these samples using this method are: Sol.A - 0.34 mg/l; Sol. B - 2.05 mg/l; Sol. C - 1.15 mg/l.

Lab 22 No comments.

Lab 23 As indicated on the report sheet, we used the methylene blue procedure sent with the sample. This procedure differs in one respect from the one which we normally use, namely, the omission of the acid water wash. Working with standards, we found the results to be very slightly different, but probably not significantly so.

Also in working with standards, we compared readings with a Coleman Junior and Beckman D.U. spectrophotometer. It would appear that the DU with 1.0 cm cells is definitely better than the Coleman Junior. When we used large cells in the Coleman, the curve was even more pronounced and different from the line given by the DU.

Lab 24 Replicate extraction on standards seems desirable in order to establish a good working curve; however, single samples extracted on successive days checked quite well.

Lab 25 Excellent repeatability. Used red filter on Sensitivity 4.

Lab 26 Curve does not follow Beers' Law. Results are taken from curved line graph rather than arbitrary straight line graph. Precision very satisfactory regarding duplication of standards.

Lab 27 See Method A[1]

Lab 28 This lab has only recently received requests for surfactant tests. Have not yet compared "M-B" with other methods. This method appears to become somewhat erratic, and the standard curve deviates considerably at levels above .15 mg. One minor deviation in technique was used. The cotton pledgets were placed in small filter funnels (35 x 50 mm) in the volumetric flasks instead of in the sep' funnels. This allowed less loss of chloroform in subsequent extractions.

Lab 29 Two cell lengths used - one selected which is in best part of curve. Result: Sample A - 0.42 mg/l; Sample B - 1.88 mg/l; Sample C - 1.12 mg/l.

Lab 30 No comments.

Lab 31 The initial spectrophotometric readings of standards and samples were unstable and decreased considerably before reaching stability. The initial readings were used for preparing the standard curve and for determining the amount of detergent because a more uniform curve was obtained.

Lab 32 It is felt that an additional extraction would be desirable on concentrations exceeding 0. 2 ppm.

Lab 33 Filter #660 (limits of 635-720) gave a smooth curve; filter #600 (limits of 580-635) resulted in a straight line. Results were identical with both curves.

Lab 34 When the method submitted with the samples was used "as is", transmittance values for triplicate standards varied so widely that a standard working curve could not be constructed. When it was noted that considerable of the blue color in the chloroform extract was retained by the absorbent cotton filter plug, it was suspected that the erratic results might be due to variation in the amount of color absorbed by the cotton during this step of the procedure. When this step was omitted, excellent results for triplicate determinations of both standards and water samples were obtained. The results tabulated were obtained by the method submitted with the exception that the chloroform extracts were not filtered through cotton.

Lab 35 The spectrum curve was checked for the band of maximum absorption and the results agreed well with the recommended wavelength of 650 mμ. Little trouble was encountered and the method seemed short and simple. It would be advantageous to the analyst if he were furnished background material and/or references so that he may see the origin of the method and its limitations. In this manner, he may then be in a position to improve the present methods.

Lab 36 The above average is obtained by discarding the one result which is out of line.

Lab 37 Relatively simple, best method found so far.

Lab 38 No comments.

Lab 39 Clear and precise.

Lab 40 No difficulty encountered in standardization or analyzing the samples.

Lab 41 In our analysis of this surfactant sample, we have found that by taking an aliquot of a sample that contains no greater than .15 mg ABS, a more accurate reading may be had from the curve. The use of methanol to clean glassware was found very efficient.

Lab 42 Have not had any experience with the method for surfactants. We do not do them in the lab. We found this method fairly simple to run.

ANALYTICAL PROCEDURES

A procedural outline for the measurement of ABS in water, using methylene blue, was supplied along with the sample. The use of this method was not mandatory and was furnished only as a suggested procedure for those agencies which did not customarily perform this measurement or which had not previously selected a method for routine use. The final tabulation of methods employed shows 43 results obtained with the ARS method, the outline of which is reproduced in this section.

Other procedures used by cooperating agencies are also described and include modifications of the ARS procedure, the methyl green method, and the British method. Since none of these methods were used more than twice, the results obtained with these procedures are not statistically significant and no effort has been made to evaluate their performance.

METHOD A
METHYLENE BLUE, ARS MODIFICATION

Reagents

Methylene blue solution - dissolve 0.35 gms methylene blue in one liter of .01 N sulfuric acid.

Chloroform, C.P.
Sulfuric Acid, 5N

STOCK STANDARD ABS, 1.00 mg/ml

WORKING STANDARD ABS, 0.010 mg/ml

GLASSWARE:

Separatory funnels, 250 or 125 ml

Volumetric flasks, 50 ml

Filtering funnels

Pipettes, assorted sizes

Preparation of Standard (Alkyl Benzene Sulfonate) Solutions

Stock Standard: Weigh out 1.602 grams of the Primary Standard ABS powder, transfer quantitatively to a 1.0 liter volumetric flask and add 500 ml of distilled water. Swirl gently until all of the powder is dissolved, let stand for one-half hour or until most of foam breaks and then make up to mark with distilled water. This solution contains 1.00 mg/ml of ABS.

Working Standard: Pipette 10.0 ml of the stock standard into a 1.0 liter volumetric flask and make up to mark. This solution contains 0.010 mgs/ml of ABS. Prepare fresh daily.

Preparation of Standards

1. Add 0, 1.0, 2.0, 5.0, 10.0, 20.0 and 25.0 ml of WORKING STANDARD ABS to separatory funnels and make up to 100 ml with distilled water. These standards contain 0, .01, .02, .05, .10, .20 and .25 mg of ABS.

2. Add three 100 ml aliquots of Sample A to each of three separatory funnels. Repeat for Samples B and C.

3. Add 1.0 ml of 5N sulfuric acid and 5.0 ml of methylene blue solution to each separatory funnel and mix.

4. Add 10 ml of chloroform to each funnel, invert and shake once a second for 25 seconds. Allow the chloroform layer to separate.

5. Draw off the chloroform layer and filter through a plug of absorbent cotton into a 50 ml volumetric flask. Repeat the extraction twice more, using 10 ml portions of chloroform, collecting the extracts in the same flask.

6. Rinse the cotton plugs with chloroform into the 50 ml volumetric flask, make up to mark with chloroform, mix well and let stand for 5-10 minutes.

7. Read the optical density of the Reagent Blank and Standards against chloroform as a reference blank at 650 mμ in a suitable photometer or spectrophotometer and prepare a standard curve.

8. Read the optical density of each sample in a similar manner and calculate mg/l of ABS in each portion. Report all results to the second decimal place.

METHOD A[1]
METHYLENE BLUE, MODIFIED

Employs same reagents as Method A

1. Transfer 100 ml sample, or smaller volume made up to 100 ml, to a 250 ml glass stoppered bottle.

2. Add 1.0 ml of 5N sulfuric acid and 5.0 ml of methylene blue solution. Mix and add 25.0 ml of chloroform.

3. Stopper the bottle and shake for 30 seconds (75 excursions) and allow the phases to separate.

4. Withdraw between 10 and 15 ml of the chloroform phase by inserting a Mohr pipette through the water phase into the chloroform layer, keeping the upper end of the pipette closed until the tip is in the chloroform to minimize the withdrawal of water.

5. Drain all but about 1 ml of the chloroform in the pipette into a 1 inch test tube and add about 2 gms of anhydrous sodium sulfate and dry by shaking.

6. Allow to stand about 5 minutes and decant the supernatant liquid into a photometer cell.

7. Prepare a standard curve by treating known quantities of ABS in the same manner. Read at 650 mμ.

METHOD A[2]
METHYLENE BLUE, MODIFIED

Employs same reagents as Method A. Procedure same as Method A except that cotton plugs were omitted. Chloroform extracts were not filtered in any way.

METHOD B
METHYL GREEN PROCEDURE

Reagents

Methyl green solution - dissolve 0.50 gms of methyl green in distilled water and dilute to 100 ml.

Glycine - Hydrochloric Acid Buffer (pH 2.5) dissolve 7.5 gms of glycine and 5.8 gms of sodium chloride in distilled water and dilute to one liter. Dilute this solution with approximately 0.10 N hydrochloric acid to produce pH 2.5. Add 3 drops of benzene as a preservative and store in refrigerator. (If bacterial growths appear in the solution, discard and prepare a fresh solution).

Dilute buffer solution - dilute 75 ml of the concentrated buffer to 250 ml with distilled water. Prepare fresh as needed.

Benzene, Reagent Grade

DILUTE WORKING STANDARD ABS - Contains .0025 mg/ml ABS.

GLASSWARE:

Separatory funnels, 125 ml

Medicine droppers (or equivalent)

PREPARATION OF STANDARDS:

1. Pipette exactly 0, 2.0, 5.0, 7.0, 10.0, 15.0 and 20.0 ml of DILUTED WORKING STANDARD ABS to 125 ml separatory funnels and add distilled water to make 20 ml in each funnel. These standards are equivalent to 0, .005, .0125, .0175, .025, .0375 and .050 mg ABS.

2. Choose an aliquot of sample such that it contains not more than 0.050 mg total ABS (less than 20 ml) and transfer to a 125 ml separatory funnel. Make up to 20 ml with distilled water.

3. Add concentrated buffer to each standard and sample. Adjust pH to 2.5 (for most samples 10 ml is sufficient).

4. Add 2.0 ml of methyl green and mix by swirling.

5. Add exactly 40.0 ml of benzene and shake for one minute. Allow the benzene layer to separate for one half hour. Swirl the funnel occasionally to insure dispersion of the methyl green - ABS complex in the solvent layer.

6. Draw off water layer carefully, taking care not to allow any benzene to escape. Add 15 ml of dilute buffer solution and shake 75 - 100 times.

7. Allow the benzene layer to separate and let stand for one hour with occasional swirling of the funnel to insure dispersion of the methyl green - ABS complex in the solvent layer.

8. Remove a sufficient volume of the benzene leyer with an eye dropper to fill the photometer cell (avoid inclusion of any water) and obtain readings at 615 mμ on a suitable photometer or spectrophotometer. Draw a standard curve and calculate concentration of ABS.

METHOD C
BRITISH METHOD

Reagents

Alkaline phosphate solution: Dissolve 10 gm of reagent grade disodium hydrogen phosphate (anhydrous) in 500 ml of distilled water. Adjust to pH 10 by addition of 1% sodium hydroxide and make up to 1.0 liter with distilled water.

Neutral methylene blue solution: Dissolve 0.35 gm methylene blue in distilled water and make up to 1.0 liter with distilled water.

Acid methylene blue solution: Dissolve 0.35 gm of methylene blue in 500 ml of distilled water, add 6.5 ml of conc. sulfuric acid and make up to 1.0 liter with distilled water.

Chloroform: Reagent Grade

WORKING STANDARD ABS, 0.010 mg/l of ABS

GLASSWARE:

Separatory funnels, 250 ml

Volumetric flasks, 50 ml

Filtering funnels

Pipettes, 5 and 10 ml

Absorbent cotton

Stirring rods

PREPARATION OF STANDARDS

1. Add 0, 1.0, 2.0, 5.0, 10.0, 20.0 and 25.0 ml of WORKING STANDARD ABS solution to 250 ml separatory funnels using volumetric pipettes and make up to 100 ml with distilled water. These standards contain 0, 0.01, 0.02, 0.05, 0.10, 0.20 and 0.25 mg of ABS.

2. Choose an aliquot of sample such that it contains not more than 0.25 mg/l of ABS and place in a 250 ml separatory funnel. Dilute to 100 ml.

3. Add 10 ml of alkaline phosphate solution and 5.0 ml of neutral methylene blue to each funnel and mix.

4. Add 15.0 ml of chloroform to each funnel, shake gently and evenly twice a second for 1 minute. Allow the chloroform layer to separate, breaking up any emulsion formed in the funnel by gentle agitation with the flattened end of glass stirring rod.

5. Run the clear chloroform layer into a second separatory funnel containing 110 ml of distilled water and 5.0 ml of acid methylene blue solution. Rinse the first separatory funnel with 2.0 ml of chloroform and add to the second separatory funnel.

6. Shake the second separatory funnel as in 4 and allow the layers to separate. Filter the chloroform layer through a small funnel plugged with cotton into a 50 ml volumetric flask.

7. Repeat from Step 4 with two further 10 ml portions of chloroform and make up the combined extracts in the 50 ml volumetric flask to the mark with chloroform.

8. Read the optical density of the Reagent Blank and Standards against chloroform as a Reference Blank at 650 mμ in a suitable photometer or spectrophotometer and prepare a standard curve.

This report was prepared by

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